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Dear editor,

We are writing to bring to your attention some clarifications and minor corrections that we believe should be made to a recent publication by Kadam et al.[1] on the monomolecular cracking of propane and n-butane. We first congratulate the authors on the accomplishment of this fine experimental work. In their study, IR operando spectroscopy was used to measure the coverage of Brønsted acid sites by propane and n-butane during monomolecular cracking, and these measurements were used to extract intrinsic rate coefficients and activation barriers for the overall rate of cracking. This work represents a major advance toward the understanding of the effects of zeolite structure on the intrinsic kinetics of monomolecular cracking. However, we believe that a few points made by the authors in reference to our work, which deals with the effects of zeolite structure on intrinsic kinetics for n-butane and n-hexane cracking and dehydrogenation using a combination of experimental measurements and Monte Carlo simulations,[2,3,4,5] which has investigated the effects of zeolite structure on intrinsic kinetics for butane cracking and dehydrogenation using a combination of experimental measurements and Monte Carlo simulations, need additional clarification. We would also like to highlight some key consistencies between our reported results and those of Kadam et al.

We begin by discussing consistencies between our reported intrinsic activation barriers for cracking of n-butane and those reported by Kadam et al.[1] Kadam et al. have reported a single activation energy of ~187 kJ mol^{-1} for the overall rate of cracking for the four zeolites that they investigated (FER, TON, CHA and MFI). We have calculated the intrinsic activation parameters corresponding to the overall rate of cracking using activation parameters corresponding to individual cracking pathways reported in our previous work;[2] these values along with those reported by Kadam et al. are given in Table 1. It can be seen that the intrinsic activation energies we have determined for FER, TON and MFI (we did not investigate CHA) range from 179 kJ mol^{-1} for FER to 184 kJ mol^{-1} for MFI, and that all values reported in our

work well as in that of Kadam et al. are within the experimental uncertainties reported by each set of authors. In addition, the activation entropies are very similar and for MFI are within experimental error between the two studies. These similarities indicate that our method of extracting intrinsic activation barriers from experimental rate measurements combined with adsorption thermodynamic parameters, determined using Monte Carlo simulations, provides an accurate estimate of the intrinsic activation barriers of monomolecular cracking of light alkanes, in particular for the activation energy.

Table 1. Values of the intrinsic activation energy and entropy for the overall rate of n-butane cracking reported by Kadam et al.,[1] and calculated using barriers corresponding to individual cracking pathways reported by Janda et al.[2]

	Activation energy (kJ mol^{-1})[a]		Activation entropy (J mol^{-1} K^{-1})[a]	
	Kadam et al.[1]	Janda et al.[2]	Kadam et al.[1]	Janda et al.[2]
FER	187(2)	179(7)	12(4)	-7(9)
TON	187(2)	180(7)	10(4)	-8(9)
CHA	187(2)	--[b]	-6(2)	--[b]
MFI	187(2)	184(7)	-5(2)	-6(9)

[a]Numbers given in parentheses correspond to twice the standard error reported by Kadam et al. and to 95% confidence intervals reported by Janda et al.
[b]Not measured

We next clarify and correct some minor errors in the descriptions of our previous conclusions[2] given by Kadam et al.[1] The authors of this paper state that we have suggested based on combining molecular simulations and experimental cracking rate measurements that structure-activity relationships are explained in general by changes in the intrinsic activation energies, and not the intrinsic activation entropy. In fact, our conclusions regarding this subject depend on the monomolecular reaction pathway and on the alkane in question. Similar to Kadam et al., for n-butane central cracking we proposed that the intrinsic rate of reaction is controlled by the intrinsic activation entropy, which becomes less negative as the confinement increases for zeolite structures possessing 10-MR channels and differing in the size and abundance of intersections or cages. On the other hand, the changes in the intrinsic rate of *dehydrogenation* appear to depend more strongly on the intrinsic activation energy, although this dependence is

irregular due to enthalpy-entropy compensation for this reaction pathway. For n-hexane consumption over FAU, MOR, and MFI we found, using previously reported kinetic data[6] combined with CBMC-calculated adsorption properties, that the overall rate of consumption of n-hexane (cracking as well as dehydrogenation, a reaction not investigated by Kadam et al.) is controlled by the intrinsic activation energy, and that both the intrinsic activation energy and entropy decreased with increasing confinement. Kadam et al. also state that their results are inconsistent with our "predictions that the [...] zeolite topology primarily influence[s] the intrinsic activation energy and not the activation entropy." In fact, our actual conclusion was that the zeolite topology influences both the activation entropy and enthalpy, both for n-hexane and for n-butane.

Finally, Kadam et al.[1] have pointed out that "The consideration of explicit models for the hydrogen bond could improve the agreement with experiments," We believe that they are referring to the agreement between the intrinsic activation parameters that they have determined experimentally with those that we have determined using a combination of experimental measurements of rate data and calculated values of the thermodynamic adsorption enthalpy and entropy. Kadam et al. have also suggested that it is important to consider the "directionality of the H-bond" between the alkane and acid site in determining adsorption enthalpies and entropies. As pointed out in our recent Minireview,[3] we have attempted in ref 2 to account for the interaction of the proton with the reactant-state alkane (i.e., alkane molecules adsorbed at Brønsted protons) in CBMC simulations by modifying the Lennard-Jones force field parameters for the oxygen atoms attached to the Al atom. The accuracy of this potential is confirmed in our recent work[7] by comparing CBMC-calculated values of the adsorption enthalpy and entropy for reactant-state alkanes with experimentally measured values for several zeolite structures (MFI, TON, FER, MWW, MOR, KFI, and FAU). We note that a specific and explicit model to capture the directionality of hydrogen bonds may be difficult given the tendency of the proton to move

rapidly amongst the four oxygen atoms at reaction temperatures. We have, therefore, opted for an effective potential in the abovementioned work by treating the four oxygen atoms as equivalent.

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